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Strategy of alternating bias voltage on corrosion resistance and interfacial conductivity enhancement of TiCx/a-C coatings on metallic bipolar plates in PEMFCs

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ABSTRACT

Proton exchange membrane fuel cells (PEMFCs) are deemed to be a promising renewable energy for variety of applications. However, metallic bipolar plates, one of key components in PEMFCs, still suffer from severe corrosion and degradation of interfacial conductivity under the humid and acid operating condition. Herein we proposed a novel strategy to enhance interfacial conductivity and corrosion resistance of TiCx/a-C coatings for metallic bipolar plates by alternating substrate bias voltage during the deposition process. The effects of the alternating substrate bias voltage strategy on the composition and morphology of the multilayered TiCx/a-C coatings had been explored. Both the corrosion resistance and the interfacial conductivity of the multilayered TiCx/a-C coatings were improved with more alternating periods of bias voltage. The effects of the enhanced performance had been discussed, and it was found that the alternating bias voltage strategy will restrain the columnar structures in the a-C layers and promote the generation of sp^2-rich clusters on the surface. This versatile strategy based on moderately alternating cycles of substrate bias voltage exhibits great potential in many applications.

1. Introduction

As one kind of promising energy generator with low operating temperature, low emission and high efficiency [1,2], proton exchange membrane fuel cells (PEMFCs) have attracted substantial academic interest on account of their potential applications in many fields, which include but are not limited to automobiles [3–5], drones [6], military equipment [7], and stationary power stations [8]. However, the commercialization of PEMFCs still suffers from fairly high cost and limited durability of stack under aggressive operating conditions [9].

Typically, PEMFCs stack is composed of membrane electrode assemblies, bipolar plates (BPPs), and seals. Metallic BPPs, one of key multifunctional components in PEMFCs, occupy over 80% of the weight and 45% of the cost in PEMFCs stack [4,10,11]. The corrosion resistance and interfacial conductivity performance of BPPs are crucial for the PEMFCs stack performance [1]. In the past decade, stainless steel has been regarded as the alternative material for BPPs [3,4,11,12]. Hence, BPPs are required to possess excellent corrosion resistance and interfacial conductivity under humid and acid operating condition. Up to now, tremendous efforts have been made for amorphous carbon (a-C) films coated on BPPs due to their excellent corrosion resistance and admirable interfacial conductivity with gas diffusion layer [13–15]. Yi et al. [16] used closed field unbalanced magnetron sputter ion plating method to deposit a-C films on stainless steel 304 BPPs. The interfacial contact resistance (ICR) value was 5.4 $m\Omega\,cm^2$ at 1.5 MPa. However, the columnar structures and pinholes, usually generated in the a-C coatings during the deposition process, easily lead to the so-called pitting corrosion [17], which is harmful to the electrochemical stability of BPPs and comprehensive performance of PEMFCs stack.

So far, multilayer coatings have been widely adopted to suppress columnar structures and improve corrosion resistance. Tüken and coworkers [18] used the cyclic voltammetry technique to obtain the multilayer coatings by synthesis of thin polyphenol film on the polypyrrole layer. Compared with single layer coating, the multilayer coatings showed barrier effect and provided a much effective protection of mild steel for much longer periods in the corrosion tests. Barshilia et al. [19] used the reactive direct current (DC)

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magnetron sputtering method to deposit TiN/NbN multilayer coatings. The corrosion behaviors of the multilayer coating with a thickness of ~1.5 μm were measured and the results revealed that the corrosion resistance was increased with number of interfaces in the coatings. Zhang et al. [20] adopted arc ion plating technique to deposit the sandwich-like Cr/CrN/Cr multilayers coatings on stainless steel. Compared with the bare substrate, the corrosion current density of the multilayer coatings decreased by one order of magnitude. After potentiostatic polarization under simulated cathode environment, the ICR values increased from 35 mΩ cm^2 to 80 mΩ cm^2. Even so, multilayer coatings fabricated by different materials may bring out the so-called local galvanic corrosion due to the perforated pinholes in the coatings [17,21]. Hence, a new deposition strategy is a necessity for anti-corrosive and conductive coatings without columnar structures in consideration of the operating condition of PEMFCs.

Here, we propose a novel and effective strategy to deposit compact TiCx/a-C multilayered coatings. To be specific, the multilayered TiCx/a-C coatings are deposited layer by layer with alternate substrate bias voltage during DC magnetron sputtering process. In each alternating cycle, the higher substrate bias voltage may bring out higher flux of energetic particles in the plasma and enhance the intensity of the bombardment and thus suppress the generation of columnar microstructures and pinholes. The superiority of alternating substrate bias voltage strategy is confirmed by the enhanced corrosion resistance and interfacial conductivity of TiCx/a-C coatings consisting of alternating 150 V a-C layer and 600 V a-C layer. The optimized TiCx/a-C coated BPPs are promising for the commercialization application of PEMFCs. In addition, the proposed strategy in this study opens a new door to anti-corrosive applications and advanced energy materials.

2. Experimental

2.1. Sample preparation

Commercial stainless steel 316L (SS316L) sheets (Cr:16.21 wt.%, Ni:9.50 wt.%, Mo:3.22 wt.%, Co:0.42 wt.%, Mn:1.47 wt.%, Si:0.34 wt.%, Cu:0.21 wt.%, V:0.04 wt.%, Fe: balance) with a diameter of 60 mm and single crystalline (110) silicon wafers were prepared as substrates. Prior to sputtering, substrates were ultrasonically cleaned in ethyl alcohol, acetone and deionized water and then a plasma blower was used to dry the substrates. After that, substrates were fixed on the sample carousel in front of the targets with a distance of 130 mm in the self-designed balanced DC magnetron sputtering system. The coating system was equipped with two high purity graphite targets (99.99%) and two high purity titanium targets (99.99%). And the chamber was firstly vacuumed to get a background pressure below 5.0E-3 Pa. During the sputtering process, argon (99.9%) was introduced as the sputtering gas. As illustrated schematically in Fig. 1a, before the deposition, the plasma cleaning was carried out to get a cleaner and more active surface. Then the protective titanium seed layer was deposited, as shown in Fig. 1b. After that, the TiCx transition layer was deposited immediately by decreasing the sputtering current of titanium targets and graphite targets at the same time. Afterwards, the alternating substrate bias voltage strategy was introduced to deposit the multilayered a-C coatings, as depicted in Fig. 1d–f. The a-C layers were deposited layer by layer by alternating the negative substrate bias voltage of 150 V and 600 V by n periods (n = 0, 5,10,15), and the total deposition time of a-C multilayered coatings was 2 h. The detailed parameters of the multilayer TiCx/a-C coating and the a-C layers were given in Tables 1 and 2.

2.2. Coating characterization

In order to explore the effects of alternating substrate bias voltage strategy on the morphology, atomic force microscope (AFM, Dimension Icon, Bruker, USA) and ultra-high resolution scanning electron microscope (SEM, MAIA3, TESCAN, Czech Republic) were used to evaluate the surface and cross-sectional morphology of TiCx/a-C multilayered coatings. X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, SHIMADZU/Kratos, Japan) was introduced to detect the composition as well as the atom binding state of TiCx/a-C coatings before and after corrosion.

In order to estimate the corrosion resistance of TiCx/a-C coatings, electrochemical experiments were carried out with the help of a commercial electrochemical workstation (Corr-Test 310, China) under the simulated PEMFCs cathode operating condition (pH = 3 H_2SO_4 solution containing 0.1 ppm HF with air bubbles at 80 °C), including the potentiodynamic polarization (scans from −0.6 V to +1.0 V at 0.1 mV/s, vs. Ag/AgCl), potentiostatic polarization at 0.6 V (vs. Ag/AgCl, abbreviated as 0.6 V polarization below) for 24 h and the high potential 1.6 V potentiostatic polarization (vs. SHE, abbreviated as 1.6 V polarization below) for 1 h. It should be mentioned that the high potential 1.6 V polarization tests are significant because the severe high potential electrochemical corrosion is inevitable during the vehicle start-stop condition [22,23]. Electrochemical impendence spectroscopy (EIS) was also employed to evaluate the corrosion resistance of bare substrate and coated samples. Concretely, the EIS experiments were carried out at a potential of 0.6 V (vs. Ag/AgCl) with an amplitude of 10 mV over a wide range of frequency from 0.01 Hz to 100 kHz in the simulated PEMFCs cathode environment. Prior to all the electrochemical corrosion tests, the electrochemical workstation was required running for 1 h to stabilize at open circuit potential. Additionally, the electrochemical tests were carried out at least three times.

ICR is another important parameter to evaluate the interfacial electrical conductivity of BPPs. A commercial micro-ohm meter (ZY9858, China) was used to measure the ICR value between the coated samples and gas diffusion layer (commercial TGP-H-060 carbon papers) under a compaction force of 1.4 MPa, which was considered as the typical assembly pressure in PEMFC stack. And the detailed testing procedures were reported in our previous work [24].

3. Results and discussion

3.1. Effects of alternating bias voltage on the morphology

Fig. 2 shows the three-dimensional morphological AFM images and corresponding root-mean-square (RMS) roughness of TiCx/a-C coatings with different alternating bias voltage periods. The RMS roughness is calculated by the NanoScope Analysis 1.40 software. As shown in Fig. 2, the topography of the TiCx/a-C multilayered coatings is composed of many hilly pinnacles. As the increase of alternating bias voltage periods, the number of hillocks decreases. Without alternating bias voltage (n = 0), the RMS roughness is the highest, i.e. ~1.28 nm. As the alternating periods further increase to 5 and 10, the RMS roughness is decreased slightly to ~0.89 and ~0.87 nm, respectively. And the sample with the highest alternating bias voltage periods has the lowest RMS roughness of ~0.71 nm.

The decreased RMS roughness of TiCx/a-C coatings is attributed to the effect caused by the alternating bias voltage strategy. In this study, the TiCx/a-C coatings are deposited in a balanced magnetron sputtering system at room temperature. It is well accepted that the higher bias voltage will bring out the higher energy state of particles in plasma and undoubtedly, the more intense bombardment comes into being from energetic particles [25–27]. Hence, in an